

CHAPTER 12

Matrix Spikes, Matrix Spike Duplicates, and Matrix Duplicates

12-1. Introduction.

a. **Matrix spike (MS), matrix spike duplicate (MSD), and matrix duplicate (MD)** results are examined to evaluate the impact of matrix effects on overall analytical performance and the potential usability of the data. A matrix spike is a *representative* environmental sample that is spiked with target analytes of interest *prior* to being taken through the entire analytical process in order to evaluate analytical bias for an actual matrix. A matrix duplicate is a collocated (e.g., a VOC soil sample) or a homogenized sample that is processed through entire analytical procedure in order to evaluate overall precision for an actual matrix. Duplicate or replicate matrix spikes are also used to evaluate overall precision.

b. Matrix spike recovery failure and poor precision may arise because of (i) poor sampling technique, (ii) inadequate homogenization, or (iii) from matrix effects associated with the preparatory or determinative portion of an analytical method. For example, inappropriate sample collection and handling procedures for VOC soil samples (e.g., as described in Method 5030) may result in variable losses of VOCs, giving rise to poor precision and low bias. Sludges, clayey soils or sediments, multi phasic samples, and samples with macroscopic particles of analytes such as explosives and metals, may defy homogenization attempts during sample preparation or compositing procedures used for sample collection, giving to unacceptable duplicate precision or matrix spike recoveries.

Note: In this document, sample heterogeneity arising from the spatial or temporal distribution of the analytes in a study area is viewed as a characteristic of the environmental population being sampled and not as an “interference” that the method of analyses must be optimized to address.

12-2. Interpretation of Matrix Spike and Duplicate Results.

a. In general, when evaluating accuracy using matrix spike recoveries, a matrix effect is inferred when (i) all instrument and method QC samples (the LCSs and CCVs) are acceptable, (ii) the spiking concentration for the matrix spike is high relative to the **native analyte** concentration, and (iii) the recovery of the matrix spike does not fall within the laboratory’s corresponding statistical range for *laboratory control samples*. Similar reasoning applies to the evaluation of precision using RPDs for MS/MSDs and MDs results. Namely, an interference is inferred when (i) instrument and method QC is in control, (ii) the native analyte concentrations are sufficiently high (e.g., above the quantitation limits), and (iii) some measure of precision (such as the RPD) exceeds the corresponding statistical LCS limits.

b. Laboratory and project documents (e.g., laboratory standard operating procedures and QAPPs) often state that the presence or absence of matrix effects is determined by establishing statistical control ranges using *MS* rather than *LCS spike* recovery data. Once the MS control limits are established, a matrix effect is subsequently inferred for a batch of environmental sam-

ples if an associated matrix spike recovery falls outside of the statistical MS control range (rather than outside of the LCS control range). *This approach will typically be inappropriate!* In order for this strategy to be viable, the matrix used to establish the MS control range must be relatively uniform, similar in composition to the environmental matrix of interest, and known to lack significant interferences.

c. Because of the variety and complexity of environmental matrices, it is usually impractical for environmental production laboratories to establish matrix-specific control limits. Most (if not virtually all) environmental laboratories that maintain statistical MS control ranges, establish MS limits by method rather than by matrix. For example, groundwater, surface water, rain water, and waste water are often erroneously considered to be the sample “matrix” for the purpose of calculating statistical MS control limits because the samples are processed using the same aqueous preparatory and determinative methods. Furthermore, the MS control ranges are frequently calculated using MS recoveries that have been impacted by matrix effects. *These problems frequently result in very wide MS control limits that are difficult to interpret and frequently do not satisfy project objectives.* Furthermore, since the MS control ranges are often calculated using spiked samples affected by significant matrix interferences, the absence of a matrix effect is not demonstrated when a MS recovery for a batch of environmental samples falls within the MS recovery range. At best, the result may demonstrate that a matrix effect (if present) is *no larger than is typically observed* for a variety of matrices analyzed by the same preparatory and determinative method.

d. In general, matrix spike control limits are not available from environmental production laboratories as “off-the-shelf” commodities but must be established on a project-specific basis. In order to obtain representative matrix spike control limits, a relatively large number of matrix spike samples (e.g., 20 to 30 samples) must be taken from each environmental medium in each project study area. *When a project’s matrix spike acceptance ranges are established solely upon the basis of a laboratory’s statistical MS control limits and these limits were developed using MS recoveries from non-project related media or dissimilar matrices that have been impacted by interferences, then the matrix spike control limits will probably be inappropriate.* Before proceeding with the data evaluation, assess the validity of the matrix spike acceptance limits (e.g., determine whether the acceptance ranges are unrepresentative or too wide to satisfy project’s data objectives). A strategy for approximating statistical matrix spike control ranges using LCS recovery data is presented in Paragraph 12-3

e. Lastly, it should be noted that matrix spike recoveries are evaluated, at least potentially, to fulfill two separate objectives: (i) *To determine whether or not matrix effects exist* and (ii) *to determine whether or not project-specific objectives for accuracy were satisfied for the analytes in the matrices of interest.* The distinction between the two objectives is somewhat subtle but important to recognize when qualifying data because data are frequently qualified (e.g., as estimated) on the basis of the second objective rather than the first.

f. To illustrate the evaluation of matrix spike and LCS results, assume that a laboratory’s statistical control range for LCS recoveries for aqueous lead analyses is 80–120%, the project-required acceptance range for MS recoveries is 50–150%, and three separate sets (batches) of samples were analyzed with associated MS recoveries of 90, 65, and 40%. Assume that the

spiking concentrations for all three MS samples are high relative to the native analyte concentrations and QC is otherwise acceptable. Since the 90% MS recovery lies within the statistical LCS acceptance limits, this recovery suggests the absence of any matrix effects. Since the MS recovery of 65% falls well outside of the LCS statistical acceptance range, the recovery is indicative of a matrix effect that is within the project-required tolerance for accuracy (50–150%). Although the recovery is indicative of matrix interference, data qualification would not necessarily be required. The recovery of 40% is indicative of a matrix effect that is greater than the project-required tolerance for matrix effects. At a minimum, data qualification would typically be required.

12-3. Estimating Statistical Matrix Spike Recovery Ranges.

a. If the spiking concentration for the MS is at least twice as large as the native analyte concentration, the laboratory's in-house statistical control or warning limits for LCS recoveries can be used to establish acceptance limits for MS recoveries:

$$\langle \%R \rangle \pm L_{95\%} (100 / \langle \%R \rangle) (\langle \%R \rangle / 100 + C_B / C_S) \quad (12-1)$$

$$\langle \%R \rangle \pm L_{99\%} (100 / \langle \%R \rangle) (\langle \%R \rangle / 100 + C_B / C_S) \quad (12-2)$$

b. As defined in Chapter 11-6, [%R] is the mean LCS recovery, $L_{95\%}$ is the half width of the LCS warning range and $L_{99\%}$ is half the width of the control range. The variable C_B denotes the native analyte concentration (i.e., the measured pre-spike sample concentration) and C_S denotes the calculated spike concentration in the sample matrix (i.e., the analyte concentration added to the sample matrix). If method bias is not significant (i.e., [%R] is near 100%), then the following equations may be used to estimate the MS acceptance ranges:

$$\langle \%R \rangle \pm L_{95\%} (1 + C_B / C_S) \quad (12-3)$$

$$\langle \%R \rangle \pm L_{99\%} (1 + C_B / C_S) \quad (12-4)$$

c. For example, if the LCS acceptance range is 80–120% (i.e., $100\% \pm 20\%$) and the spike concentration is twice the native analyte concentration, then the acceptance range for the MS recovery is as follows:

$$100 \pm 20\% (1 + 1/2) = 100 \pm 30\% = 70\text{--}130\%$$

d. Therefore (in this example), if the LCS recovery for a batch of environmental samples falls within 80–120% but the recovery of the associated matrix spike does not fall within 70–130%, then a matrix effect would be demonstrated.

e. The acceptance range for MS recoveries may be set equal to the acceptance range for LCS recoveries when the MS spike concentration is much higher than the native analyte concentration (e.g., by a factor of five to ten) or when it is desirable to establish a conservative (i.e., a more narrow) MS acceptance range.

Note: Since two measurements are required to calculate a MS recovery (the “pre-spike” and “post-spike” sample concentrations) but only one measurement is required to calculate the LCS recovery (the “post-spike” sample concentration), in order to establish MS acceptance limits from the statistical LCS acceptance limits, the random error associated with the additional MS measurement must be taken into account. (A “pre-spike” sample concentration is not measured for the LCS; since the LCS is a spiked blank, the “pre-spike” sample concentration is assumed to be zero.) The correction factors enclosed in parentheses in Equations 12.1 to 12.4 account for the additional measurement uncertainty associated with MS recovery determinations. The correction factors were calculated by assuming that the standard deviation is a linear function of concentration and give first-order approximations for the MS acceptance limits.

12-4. Criteria.

12.4.1. Representativeness.

a. Before evaluating matrix spike results, review the SAP, QAPP and similar planning documents. These documents should describe how representative matrix spikes will be selected for the environmental matrices of interest, particularly for heterogeneous matrices such as soils.

b. The composition of a matrix spike sample must be similar to that of the associated environmental samples. For example, when soil sampling is performed, the SAP should describe how the on-site geologist will select representative matrix spikes. This typically entails classification of soil type. For example, a matrix spike should be collected for a set of samples high in sand and a separate matrix spike should be collected for a set of samples high in clay. However, this does not imply that matrix spikes should be collected solely on the basis of grain size classification (e.g., sand, silt, and clay). For example, the origin of the geological formation (fill, glacial deposits, stream deposits, etc.) should also be taken into account. Therefore, unless all soil samples are being collected in a single geological formation of relatively uniform composition or matrix interference has been well characterized during prior investigations, a batch of samples should typically contain several matrix spikes (each representing a different soil type and general origin). Similarly, if only one matrix spike were collected for a set of groundwater samples but the groundwater samples were collected from two hydraulically isolated aquifers being investigated at the site (e.g., a “shallow” and a “deep” aquifer), then, in general, one should not assume that the matrix spike would be representative of the groundwater in both aquifers.

c. If the matrix spike sample for the preparation batch originates from a different project site or is suspected to be of dissimilar composition from the other samples in batch, it must not be used to qualify the other field samples. In order to consolidate small numbers of samples from different project sites, the laboratory may analyze samples from different projects together in the same preparation batch for the same parameters. However, the MS results would not be applicable to the samples collected from the other sites. Allowing the laboratory to choose the samples to be spiked often results in the selection of unrepresentative matrix samples. Similarly, matrix spikes must not be selected by field personnel in a manner that is solely designed to satisfy frequency requirements. For example, the collection of all matrix spikes on the last day of

sampling activities to satisfy a 5% frequency requirement for the collection of matrix spikes will typically result in unrepresentative matrix spike samples.

d. In general, a matrix spike sample must contain all the target analytes of interest. A subset may be used when it can be demonstrated that the subset of target analytes characterizes (i.e., represents) method performance for the remaining (unspiked) target analytes.

Note: When only a subset of the target analytes is included in the matrix spikes, project documents such as the QAPP must present a scientifically defensible rationale for not spiking the entire set of target analytes. A number of promulgated analytical methods recommend specific target analytes for the matrix spikes. Merely referencing a subset of analytes recommended in a published analytical method (e.g., the six MS compounds listed in SW-846 Method 8260B) does not constitute a scientifically defensible rationale for not spiking all the target analytes (e.g., unless the method explains why the subset of spiked analytes is representative of the remaining target analytes).

12-4.2. Frequency.

Review the appropriate project documents (e.g., the QAPP) to determine the required frequency of MSs, MSDs, and MDs. A MS and MSD or MS and MD (representative of each type of matrix analyzed) are usually required for every batch of samples processed. MD pairs are typically used for inorganics (especially metals) and MS/MSDs for organics. Matrix spikes and matrix duplicates are usually collected at a frequency of at least 5% if the matrix is relatively uniform in physical composition.

12-4.3. Acceptance Limits.

Bias and precision specifications for matrix spikes and matrix duplicates are dependent upon the DQOs of the investigation. Acceptance limits for matrix spikes and duplicates should be specified in project documents such as the QAPP. Guidance for establishing “default” acceptance limits for matrix spikes and matrix duplicates (e.g., when acceptance limits are not specified) is presented below.

12-4.3.1. Project Specific Communications.

a. The laboratory’s statistical LCS acceptance limits should not be greater than the project-required acceptance limits for matrix spikes and matrix-dependent duplicates. When this criterion is not satisfied (i.e., project-required acceptance limits are more stringent than the statistical LCS acceptance limits) and matrix spikes or matrix-dependent duplicates fail to meet the project-required acceptance limits, it is not generally valid to assume that the failures resulted from matrix effects. For example, assume that the statistical LCS recovery range is 60–140%, the project-required MS recovery range is 80–120%, and a MS recovery for a batch of environmental samples is 65%. The associated environmental samples must be qualified (e.g., using the J flag) for not meeting the project-required tolerance for accuracy. However, the associated sample results must not be qualified for matrix interference. (In this example, the MS recovery of 65% falls well within the statistical LCS acceptance range).

b. If the acceptance limits for matrix spikes are *not specified or are inappropriate* (e.g., refer to Paragraph 12-2) and the laboratory's *statistical* LCS acceptance ranges are *comparable to or more stringent* than the *project-required* LCS acceptance ranges (e.g., the warning or control ranges for the LCS recoveries fall approximately within the corresponding project-required acceptance ranges for the LCS recoveries), then approximate the statistical matrix spike recovery ranges as discussed in Chapter 12-3. Compare the calculated MS acceptance ranges and the project-required LCS acceptance ranges. Qualify the environmental data using the most extreme limits from the two sets of acceptance ranges. However, it is emphasized that this approach is applicable only if the project-required LCS ranges are greater than or equal to the laboratory's statistical control ranges.

Note: It is recommended that the ranges be rounded (e.g., to the nearest 5% or 10%) to more readily compare the laboratory's statistical acceptance range to a project-required acceptance range. It is also recommended that the laboratory's statistical limits be viewed to be comparable to the project limits, when the LCS warning range falls approximately within the project-required LCS acceptance range. Alternatively, the width of the control range should be no greater than about 1.5 times the project's acceptance range. For example, if the project-required recovery range for the LCS is 90% - 110%, then a warning range of 90% - 110% or a control range of 85% - 115% would be considered to be acceptable.

c. To illustrate the above approach, assume that a matrix spike acceptance range is not specified, the laboratory's statistical control range for the LCS is 67–113% (i.e., $90\% \pm 23$) and the project-required acceptance range for the LCS is 70–130%. The laboratory's statistical control range approximately falls within project-required LCS acceptance range. If it is assumed that the spiking concentration for the MS is at least twice as large as the native analyte concentration (e.g., which will typically result in a conservative estimate for the MS acceptance range), then, using Equation 12.4 in Chapter 12.3. In this example, the acceptance range for the MS is $90\% \pm 23\% (1.5) = 55\text{--}125\%$. (Note that if Equation 12-2 were used, the acceptance range would be only be slightly wider: $90\% \pm 23\% (1.6) = 53\text{--}127\%$.) Since the calculated MS acceptance range is 55–125% and the project-required LCS acceptance range is 70–130%, set the MS acceptance range for the project using the most extreme limits; use 55–130% as the MS acceptance range. Therefore, a MS recovery that does not fall within 65–130% is indicative of a significant matrix effect *and* the associated environmental samples would be qualified (e.g., as estimated or potentially rejected).

d. When acceptance limits for matrix spikes recoveries are *not specified or are inappropriate* and the laboratory's *statistical* LCS control ranges are significantly *wider* than the *project-required* LCS acceptance ranges, then a conservative approach is recommended. *Evaluate the matrix spike recoveries using the project-required LCS acceptance limits.* For example, if the LCS acceptance range is 80% - 120%, then the matrix spike acceptance range should be set to 80% - 120%. If LCS acceptance limits are not specified, then use the guidance presented in Chapter 11 of this document to establish a set of “default” LCS/MS acceptance limits. In general, if the MS recovery falls outside of the LCS acceptance range, then qualify the associated results as estimated or rejected. *However, it is inappropriate to attribute the unacceptable MS*

recovery solely to matrix interference. The evaluation strategies for the matrix spike and matrix duplicates are essentially the same as those for laboratory control samples described in Chapter 11.

12-4.3.2. Establishing Acceptance Limits for Matrix-Dependent Duplicates.

If acceptance limits are not specified for **matrix-dependent duplicates** (i.e., MDs and MS/MSD pairs), if appropriate, then calculate the matrix spike limits using the procedure Chapter 12.3 and set the maximum RPD equal to one half the calculated MS acceptance range. Alternatively, evaluate the RPD results using the project-required RPD acceptance limits for *laboratory control samples*. If RPD limits are not specified for laboratory control samples, set each RPD acceptance limit for matrix-dependent duplicates equal to one half of the width of the project-required recovery range for the corresponding LCS, or to the laboratory's statistical RPD acceptance limit when derived from LCS data, whichever is less. For example, if the project-required LCS recovery range is 80% - 120% and the laboratory does not maintain statistical limits for duplicate precision using LCS data, set the RPD acceptance limit for matrix-dependent duplicates to 20%.

12-5. Evaluation.

Review the standard preparation logs to verify that all target analytes were included in the matrix spike. Using the laboratory summary forms for the matrix spike and matrix duplicate results, recalculate the recovery and the RPD for at least one target analyte. Compare the calculated values to the values reported on the laboratory's summary form. The result must agree to within two significant figures. Review the Case Narrative and all of the recovery and precision results on the laboratory summary forms and note any failures.

12-6. Contractual Considerations.

a. Contractual issues may impact the review of MS, MSD, and MD data. However, contractual considerations for matrix spikes and matrix duplicates are more complex than those for blanks and laboratory control samples because the results are dependent upon matrix effects as well as sample preparation and analysis errors. For example, the heterogeneity of soil grab samples and sequentially collected groundwater samples complicates the evaluation of MS/MSD results because uniform concentrations are assumed for the native analytes. Therefore, laboratories do not typically base batch control on the results of MS, MD, or MSD samples unless a general method failure is indicated.

b. When matrix spikes or matrix duplicates grossly fail QC acceptance limits in a systematic manner, examine the Case Narrative and any laboratory communications (e.g., phone logs) included in the data package to determine if the Project Manager was notified and corrective actions other than data qualification were performed. Refer to project planning documents such as the Scope of Work for laboratory analytical services and the QAPP to determine whether corrective actions other than data qualification are required.

c. When gross failures occur and expected laboratory corrective actions are not performed, the reviewer should consult with the Project Manager to determine whether to proceed

with the PB review or to reject the data package as a whole (e.g., the laboratory may be required to reanalyze the environmental samples). Some probable corrective actions for matrix interferences are listed below:

(1) If a matrix spike recovery is unacceptable and matrix interference is suspected, then the laboratory should be expected to make a reasonable attempt to remedy the problem. Corrective action for matrix interference may include the implementation of cleanup procedures or other method modifications. For example, cleanup methods should be performed to address matrix interferences for extractable organic analyses such as the BNA, pesticides, and PCB analyses (e.g., as described in SW-846 Method 3600). The method of standard additions may be required for metal analyses. Under these circumstances, verify that appropriate method modifications were performed to minimize the matrix interference.

(2) When a MS recovery is unacceptable but matrix interference is not otherwise apparent, the MS sample would normally be reprocessed (e.g., reextracted and reanalyzed) by the laboratory to verify the effect. However, the MS sample would not be reprocessed if the failure is consistent with historical data. The matrix effect is confirmed if the second result is similar to the original result (in magnitude and direction of bias). It should be noted that some methods specify other verification procedures. For example, if low matrix spike recoveries are obtained for hexavalent chromium in soil, Method 3060A indicates that additional analyses should be performed (e.g., pH and oxidation-reduction potential) to determine whether or not the low matrix spike recovery results from reducing conditions within the environmental sample. When unacceptable matrix spike recoveries are obtained, examine the data package to determine if appropriate confirmatory procedures were implemented.

12-7. Qualification.

Data that fail quality objectives because of matrix effects may be unusable to support decisions and must be qualified. Data quality may also be adversely impacted if the matrix spike sample is not representative of the other environmental samples in the batch. Data are qualified for matrix effects primarily using the same qualification strategies for laboratory control samples. In particular, data qualification must take both magnitude and direction of bias into account. When both a MS and MSD are processed for a batch of samples, use the most noncompliant matrix spike recovery to evaluate and qualify the data. Additional guidance is presented below.

12-7.1. Matrix Spikes and Matrix Spike Duplicates.

a. For both the MS and MSD, compare the spiking levels to the concentrations of the native analytes in the sample selected for spiking. If the native concentration of a target analyte is high relative to the spiking concentration, then this may contribute a significant uncertainty to the recovery calculations; the MS recovery may not be representative of actual method performance for the matrix. In the absence of other guidance, *evaluate the MS recovery when the spiking concentration is at least two times greater than the native analyte concentration*. If environmental samples were qualified by the laboratory for matrix interference but the spiking levels are low relative to the native analyte concentrations, then the flags must be omitted. However, professional judgment is important when evaluating the native analyte concentration relative to

the spiking concentration. For example, if the spiking concentration is near but less than two times the native analyte concentration, a gross MS recovery failure (e.g., a MS recovery of 5%) is probably indicative of a matrix effect (rather than a low-spiking concentration) and the associated results must be qualified for matrix interference. In general, if the MS spiking concentration is between one and two the native analyte concentration, then data qualification is recommended only when gross MS recovery failures occur.

b. If the LCS results are acceptable, the spiking levels for the MS are high relative to the native analyte concentrations (i.e., at least two times the native analyte concentration), the matrix spike sample is representative of the other environmental samples, and the MS recovery falls outside of the acceptance limits, then significant matrix interference may exist. Qualify the *associated* sample results (e.g., environmental samples of a similar matrix collected from the same site) as follows:

(1) If all target analytes are present in the matrix spike, and the recovery of a particular analyte is unacceptable, then qualify all detections of the analyte in the associated environmental samples using the strategies discussed in Chapter 11. For example, if the MS recovery for a target analyte falls grossly below the lower recovery acceptance limit, then qualify all detections less than the AL with the X flag. Note that in those instances where it can be determined that the MS or MSD results affect only the sample spiked, qualification must be limited to this sample alone.

(2) If all the target analytes are not present in the matrix spike, then use professional judgment to determine the extent to which qualification of the non-spiked target analytes is required. In general, each spiked analyte must be clearly linked to each of the unspiked target analytes. If one of the spiked analytes clearly represents some subset of the target analytes, then qualify only the target analytes of the subset on the basis of the MS recovery. For example, if analyte “A” in the matrix spike sample is representative of the subset of target analytes {A, B, C} in the environmental samples, then qualify analytes “A,” “B,” and “C” for the environmental samples using the MS recovery of analyte “A.” However, if a clear association does not exist (e.g., and the lack of matrix interference was not demonstrated during a prior sampling event), then a conservative approach is recommended. At a minimum, qualify detections and nondetections for the unspiked analytes in the environmental samples as estimated (i.e., qualify detections with the J flag and nondetections with the UN flag). However, if the recovery of one or more of the spiked analytes is unacceptable, then qualify all of the unspiked analytes using the most noncompliant MS recovery.

c. If a MS sample is not available or is not representative of the other samples in the batch, then the performance of the method in the matrix of concern has not been well characterized. At a minimum, qualify the environmental sample results as estimated. If the data are being used to support critical decisions and method performance in the matrix of concern is not otherwise known (e.g., the environmental population of interest has not been previously sampled and the surrogate recoveries are not available or representative of the target analyte), then it may be appropriate to qualify the sample results as tentatively rejected.

12-7.2. Matrix-Dependent Duplicates.

a. Precision is typically measured using the RPDs for MS/MSD or MD pairs. MS/MSD pairs would normally be used to evaluate duplicate precision when low-level contamination is anticipated (i.e., analyte concentrations less than the MQLs) and MDs would normally be used to evaluate duplicate precision when high levels of contamination are expected. Compare the RPDs reported for all target analytes to the corresponding RPD acceptance limits.

b. Evaluate target analyte RPDs for MS/MSD pairs when the spike concentration is at least *two times* the native analyte concentration. Evaluate target analyte RPDs for MD pairs for analytes detected at or above the MQL. (The RPD is evaluated when a target analyte detection is greater than or equal to the MQL for at least one sample of the MD pair.) RPD results that do not satisfy these criteria (e.g., RPDs calculated from detections at concentrations less than the MQLs) must not be used to evaluate duplicate precision.

Note: Sometimes an acceptance criterion for duplicate precision is specified for the MQL and a different acceptance criterion is specified for concentrations that are greater than the MQL by some multiplicative factor. Evaluate the appropriateness of the duplicate precision acceptance criterion that is nearest to the decision limit prior to performing data qualification. For example, assume that the QAPP requires the maximum RPD to be 40% for results equal to or greater than five times the MQL and requires results to agree to within \pm MQL for concentrations between the MQL and 5 x MQL. Also assume that AL = 32 ppb, MQL = 20 ppb, and the following duplicate results are obtained: 20 ppb and 40 ppb. Since the duplicate results are less than 5 x MQL (100 ppb) and agree within \pm MQL (i.e., \pm 20 ppb), according to the QAPP, the results should not be qualified. However, since the MQL is near the AL and the RPD for the duplicate pair is high (RPD = 67%), the duplicate results do not demonstrate that contamination is above or below the AL. Contrary, to the criteria specified in the QAPP, qualified the associated sample results as estimated (e.g., unless quantitative statistical methods are being used to quantify the uncertainty and to compare the results to the AL).

c. If (i) the LCS results are acceptable, (ii) the spiking levels for the MS/MSD are high relative to the native analyte concentrations (i.e., at least two times the native analyte concentration) or the native analyte concentrations for the sample/MD are at least as high as the MQL, and (iii) the RPD is unacceptable, then a significant matrix effect may exist.

d. If precision is evaluated using MS/MSD pairs containing only a subset of the target analytes of interest and the analytes are representative of the set of unspiked target analytes, then qualify the sample results using the subset of target analytes in the MS/MSD. If it is unknown whether or not the subset of target analytes adequately represents the unspiked target analytes, then a conservative approach is recommended. Evaluate the unspiked target analytes using the most noncompliant RPD for the MS/MSD. However, even when duplicate precision is acceptable for the subset of target analytes in the MS/MSD, it may be appropriate to qualify all detections and nondetections of the unspiked target analytes as estimated (e.g., when statistical

analyses are not being performed to characterize the variability of these analytes in the matrix of concern).

e. When the RPD is unacceptable, qualify the associated sample results using the same strategies presented in Chapter 11 (e.g., Table 11-2). For example, when precision is evaluated using MD pairs or MS/MSD pairs and the direction of bias is unknown, then qualify all detections of the analyte in the associated environmental samples with the J flag and nondetections with the UN flag when marginal failures occur. However, when the RPD is marginally unacceptable and the direction of bias can be determined from other QC information, then qualify the detections using J+ or J- flag (instead of the J flag). For example, assume that the acceptance range for matrix spike recoveries is 80–120%, the acceptance limit for the RPD is 20%, and an RPD of 33% was calculated from matrix spike recoveries of 70 and 50%. Since the RPD is marginally unacceptable and bias is low, the associated detections would be qualified with the J- flag. However, in those instances where it can be determined that the results affect only the MD or MS/MSD pairs (and not the other samples in the preparation batch), then qualification must be limited to those samples alone.

f. It may not be possible to collect representative duplicates. For example, if duplicates are collocated samples (e.g., a pair of VOC soil samples) or cannot be homogenized because of the nature of material being sampled (e.g., multi phase wastes), then high RPDs are probably the result of sample heterogeneity rather than method performance problems in the matrix being investigated (e.g., digestates with high concentrations of dissolved salts, being analyzed for trace metals by Method 6010B, are not intermittently clogging the ICP nebulizer, giving rise to erratic results). If precision failures occur (gross or marginal) sample heterogeneity, then it is recommended that detections be qualified with the J flag and nondetections be qualified with the UN flag. The data review report must state that representative duplicates were not collected and the data user should determine whether or not the environmental sample and matrix-dependent duplicate results can be used to support project decisions.